

Dynamics of polymer thin films in supercritical carbon dioxide

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Abstract. – *In situ* neutron reflectivity and dynamic secondary ion mass spectrometry measurements were used to investigate the dynamics of polystyrene thin films in supercritical carbon dioxide (scCO₂). The results show that the large degree of anomalous swelling observed is associated with a decrease in glass transition temperature that occurs only within a narrow region of the phase diagram associated with the density fluctuation ridge in scCO₂ region. Furthermore, the plasticization effect induced by the density fluctuations was found to enhance the polymer interdiffusion by 2 orders of magnitude as the ridge was approached. Within the ridge the diffusion coefficients scale as M^2 and can be approximated by an effective William-Landel-Ferry (WLF) equation.

Currently the large-scale chemical manufacturing has been turning to “green solvent” technologies to replace organic solvents that have raised serious environmental concerns. Supercritical CO₂ (scCO₂), which has a readily accessible critical temperature (T_c) of 31 °C and a critical pressure (P_c) of 7.38 MPa, is an attractive candidate. On the other hand, since the number of polymers that are miscible in scCO₂ is very small, it is still not commonly used in polymer processing applications [1]. We have recently demonstrated that scCO₂ may serve as a “universal solvent” near polymer surfaces and in thin films within a narrow temperature and pressure regimes, known as the “density fluctuation ridge” [2]. Here we explore how the glass transition, viscosity, and chain dynamics of polymer thin films are affected by the phase diagram of CO₂ in the vicinity of the ridge. Knowledge of these properties is essential for the processing of these films as lubricants, adhesives, and multi-component coatings.

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Using neutron reflectivity (NR) we found that CO₂ could be sorbed to a large extent in polymer thin films even when the bulk miscibility of the polymers with CO₂ was very poor [2]. Films of polymers, such as polystyrene (PS) and poly (methyl methacrylate) (PMMA) were observed to swell by approximately 30% as a function of temperature and pressure near $T \approx T_c$, which are well below their glass transition temperatures ($T_g \sim 100^\circ\text{C}$). The swelling was reversible and reached a maximum at pressures and temperatures along the density fluctuation ridge that defines the maximum density fluctuation amplitude for CO₂ [3]. The functional form of the dilation amplitude followed that of the density fluctuations as a function of temperature and pressure. In addition, the NR measurements showed that uniform density films were formed with a maximum roughness less than 25 Å. Hence we concluded that the swelling did not seem to be associated with phase separation which ultimately leads to a void formation when CO₂ is rapidly evaporated as previously reported for the bulk films [4,5]. Rather, it was postulated that in order to suppress the large density fluctuations, CO₂ became solubilized in the viscous polymer films.

It is well known that the equilibrium sorption of CO₂ into the polymers plays a role as a diluent or plasticizer for the glassy polymers [6–9]. However, as will be shown later, the sorbed CO₂ amounts in the PS thin films observed at the ridge never realize in the bulk PS-CO₂ system even at high pressures, suggesting that the plasticization effect of CO₂ could be significantly enhanced by the density fluctuations of CO₂. In addition, little attention has been paid to the interdiffusion process of polymer chains in the supercritical fluids. In this paper, by combination NR and dynamic secondary ion mass spectrometry (DSIMS) measurements, we study the effects of pressure and temperature, which can control the magnitude of the density fluctuations, on the effective glass transition, interfacial roughness and chain diffusion in the swollen films. We also show that the effect could be frozen by flash evaporation of CO₂, yielding stable low density and low index of refraction films.

Thin films (approximately 500 Å thickness) of monodisperse deuterated polystyrene (d-PS) ($M_w = 957000$ g/mol, $M_w/M_n = 1.17$, Polymer Source) were spun cast onto HF etched Si wafers to study the *in situ* film quality in CO₂. For the tracer diffusion measurements, bilayers samples were prepared by using protonated polystyrene (h-PS, $M_w = 697000$, Polymer Source) and five different molecular weights of d-PS ($M_w = 94000, 155000, 250000, 404000, 690000$). All d-PS polymers were obtained from Polymer Laboratories, and the polydispersity indices, M_w/M_n , were 1.05 or less. The bottom layer (h-PS) with about 700 Å thickness was prepared by spin coating on Si wafer. The overlayer (d-PS) whose thickness was about 500 Å for NR measurements was then floated on top from deionized water. The samples were then inserted into a special high-pressure chamber designed for *in situ* NR measurements. Details of the chamber will be described elsewhere [10]. The NR measurements were performed on the NG7 neutron reflection spectrometer at NIST. DSIMS experiments were performed by both a CAMECA time of flight (TOF)-SIMS using a Ga ion beam of 15 keV with a spatial resolution of 40 Å and an Atomika DSIMS using a rastered Ar⁺ ion beam of 2 keV with a spatial resolution of 80 Å. The setup for DSIMS has been described elsewhere [11].

Figure 1 shows the NR data for a d-PS single layer ($M_w = 957000$) at $T = 36^\circ\text{C}$ and three different pressures, $P = 0.1$ MPa, $P = 8.2$ MPa ($P \sim P_c$), and $P = 34.5$ MPa ($P > P_c$). From the figure we can see that the oscillations are well defined, indicating that the roughness is relatively small. The reflectivity curves were fit with model density profiles having three free parameters: film thickness, scattering length density (SLD), and interfacial root-mean-square (rms) roughness (σ) between polymer and CO₂ layers, which was approximated by a hyperbolic-tangent function. The results are plotted in the inset of fig. 1, where we see that linear dilation (S_f) and σ reach a sharp maximum at $P = 8.2$ MPa, which lies on the density fluctuation ridge. The S_f values were calculated from the equation $S_f = (L - L_0)/L_0$, where

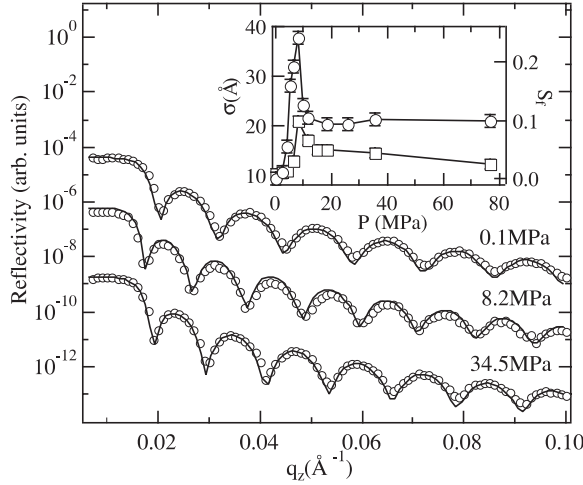


Fig. 1 – Representative reflectivity data at $T = 36^\circ\text{C}$ are shown. Consecutive reflectivities have been offset from each other for clarity. Solid lines represent the reflectivity calculated from the corresponding SLD profiles. In the inset the pressure dependence of σ (\square) and S_f (\circ) for d-PS at $T = 36^\circ\text{C}$ is shown.

L and L_0 are the measured thickness of the swollen and unswollen polymer thin films. A similar maximum in S_f was previously reported for deuterated styrene-butadiene copolymer (d-SBR) thin films in CO₂ at the same pressure and temperature, where it was shown that the dilation had the same functional form as the density fluctuation function for CO₂ [2]. Since the observed temperature was well above the T_g value of d-SBR ($T_g = -30^\circ\text{C}$), the segmental fluctuations were very fast and changes with CO₂ temperature and pressure were too small to be observed. Here the temperature is well below T_g of d-PS and we are very sensitive to any changes in the segmental fluctuations. The abrupt increase in the interfacial roughness when S_f is large indicates that a drastic increase in the chain fluctuations times also occurs at the ridge. Hence the data suggest that a CO₂-induced glass-liquid transition may be occurring. Away from the ridge at $P > 10$ MPa, the S_f and σ values decrease abruptly with increasing pressure, suggesting that the d-PS thin film undergoes vitrification again. Condo *et al.* have shown that T_g of bulk PS decreases almost linearly with the weight fraction of CO₂ (w_{co}) [9,12]. Based on the SLD parameters obtained from the NR results [13], we found that the w_{co} values at $T = 36^\circ\text{C}$ were less than 6% except for that at the ridge ($w_{\text{co}} = 14\%$ at $P = 8.2$ MPa). It should be emphasized that the w_{co} value of 14% at the ridge never occurs in the bulk PS-CO₂ system even at high pressure. The calculations [12] therefore predicts that $T > T_g$ only at the ridge, as implicated in the density fluctuation data.

In order to prove conclusively that the film undergoes a glass-liquid and/or liquid-glass transition along the ridge, we measured the tracer diffusion coefficient in PS as a function of temperature and pressure. Figure 2(a)-(c) shows the NR curves obtained at $T = 36^\circ\text{C}$ after exposure to CO₂ for two different times at three different pressures. At low pressures ($P = 2$ MPa), the NR curves show only a small increase in total film thickness without significant broadening of the interface between the d-PS and h-PS layers. This indicates that the films were still in the glassy state, even after 12 h of immersion in CO₂. In fig. 2(b), one observes a significant change in the NR curves at the ridge ($P_{\text{ridge}} = 8.2$ MPa at $T = 36^\circ\text{C}$). The σ value between the layers was estimated to be 42 ± 4 Å after only 0.5 h of immersion

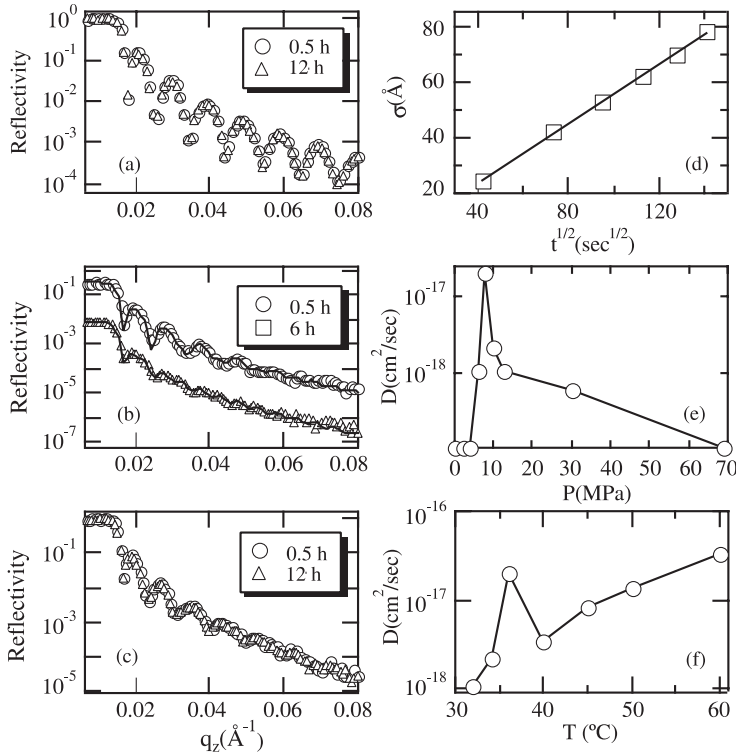


Fig. 2 – Time dependence of NR curves at different pressures and $T = 36$ °C: (a) $P = 2.0$ MPa; (b) $P = 8.2$ MPa; (c) $P = 70.0$ MPa. (d) σ vs. $t^{1/2}$ at $T = 36$ °C and $P = 8.2$ MPa. Diffusion coefficients are plotted (e) as a function of pressure at $T = 36$ °C, and (f) as a function of temperature at $P = 8.2$ MPa.

and 77 ± 6 Å after 6 h immersion. As can be seen in fig. 2(d), we find that σ scales linearly with $t^{0.5}$, indicating that the diffusion between the layers progresses as Fickian diffusion [14] with a constant diffusion coefficient (D), $D = \sigma^2/2t$. From the solid line fit to the data, we determined $D = 2 \times 10^{-17}$ cm²/s at the ridge. In fig. 2(c) we show the NR reflectivity spectra when the pressure is increased to $P = 70$ MPa and find that the diffusion does not occur within at least 12 h, indicating that the film undergoes the vitrification again. Figure 2(e) is a semi-log plot of the D values measured at different pressures. From the figure one clearly sees that D increases by almost 2 orders of magnitude as the ridge is approached and decreases sharply with increasing pressure above P_{ridge} . This data therefore provides the first direct evidence of a CO₂-induced glass-liquid-glass transition associated with the density fluctuation ridge. Since the anomalous solubility is believed to be an equilibrium phenomenon, independent of the direction of approach to the ridge [2], the dynamics were further investigated under isobaric condition at $P = 8.2$ MPa. The data is plotted in fig. 2(f) where we again find a maximum on the ridge at $T = 36$ °C. In contrast to the isothermal plot, D is seen to increase again for $T \geq 40$ °C, since, as we show later, diffusion is a temperature-activated process which has been shown previously for bulk samples [15], and some plasticization of the PS thin film occurs even away from the ridge.

Next, we further concentrate on the interdiffusion of polymer chains enhanced by density fluctuations. In order to compare the dynamics in scCO₂ with those observed in the normal

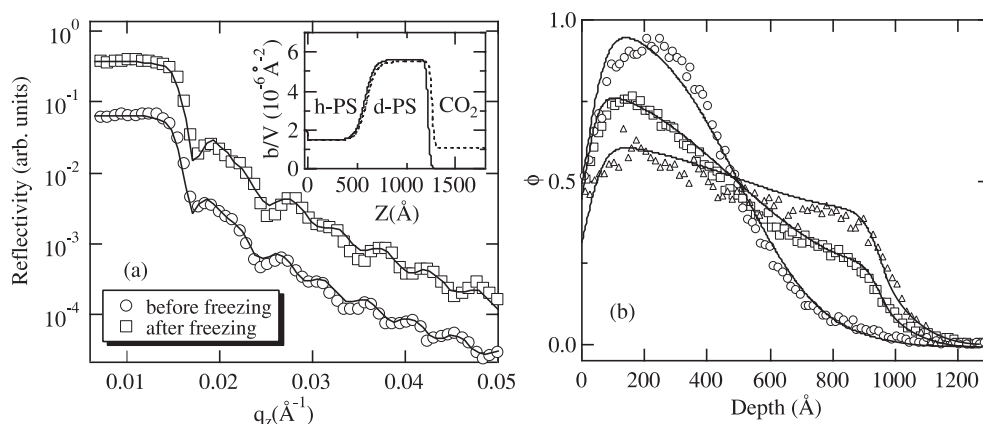


Fig. 3 – (a) NR curves before and after freezing. Solid lines are the calculated reflectivity based on the corresponding SLD profiles shown in the inset: dotted lines: before quench, solid line: after quench. (b) Concentration profiles of d-PS films of $M_w = 94000$, 250000 and 404000 allowed to diffuse into the h-PS ($M_w = 697000$) matrix.

entangled melt above T_g , we measured the diffusion coefficients along the ridge, as a function of d-PS molecular weight. NR measurements were initially conducted at other ridge conditions, *i.e.*, $T = 40^\circ\text{C}$ and $P = 9\text{ MPa}$, and $T = 50^\circ\text{C}$ and $P = 10\text{ MPa}$. However, the dynamics of the lower molecular weight d-PS polymer chains at these conditions were too fast to be studied *in situ* with NR since the diffusion appeared to be faster than the data acquisition time of approximately 1 h. We, therefore, experimented with “freezing” samples below T_g for data analysis in a manner analogous to standard diffusion measurements on these polymers where samples are annealed in vacuum ovens set at $T > T_g$ and rapidly quenched to $T < T_g$ for analysis. Bilayer samples were placed in the high-pressure chamber and immersed in scCO₂ at four different ridge conditions ($T = 36^\circ\text{C}$ and $P = 8.2\text{ MPa}$, $T = 40^\circ\text{C}$ and $P = 9\text{ MPa}$, $T = 45^\circ\text{C}$ and $P = 9.5\text{ MPa}$, and $T = 50^\circ\text{C}$ and $P = 10\text{ MPa}$) for annealing times varying from 1 to 100 h. The samples were then quickly depressurized to atmospheric pressure at constant temperature within 10 s. In order to check that the relaxation times were sufficiently long to freeze in structure once ambient pressure and temperature were reached, we compared the NR curves for an h-PS ($M_w = 697000$)/d-PS ($M_w = 94000$) film before and after the quench. The reflectivity spectra are shown in fig. 3(a). From the figure we can see that the two curves are nearly identical. The difference between them is a small shift in the wavelength of the oscillations, which corresponded to a uniform 20 Å decrease in the d-PS film thickness (from 660 Å to 640 Å after the quench). The original value at ambient conditions was 550 Å . The interfacial roughness ($\sigma = 86 \pm 6\text{ Å}$), on the other hand, is unchanged before and after the quench. In addition, the diffusion coefficient for the quenched samples obtained by TOF-SIMS was in good agreements with that obtained from the NR measurements. Hence, we concluded that the *in situ* structures can be quenched by rapid evaporation which enabled further measurements to be performed using DSIMS where the diffusion is more sensitive than NR to diffusion over larger distances.

In fig. 3(b) we show the DSIMS concentration profiles, as determined from the D[−] ion intensity, for bilayer samples of different d-PS molecular weights, annealed for 10 h at $T = 50^\circ\text{C}$ and $P = 10\text{ MPa}$ and then quenched. The solid lines, which provide a good fit to the data, correspond to the solution of the Fickian equation (convoluted by a Gaussian function

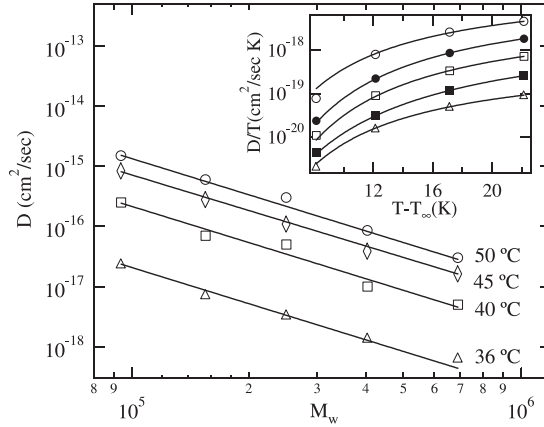


Fig. 4 – D vs. M_w with $L_0/R_g = 3$ along the ridge. Solid lines are fits with slopes of -2.0 . In the inset, D/T vs. $T - T_\infty$ for different M_w : 94000 (\circ), 155000 (\bullet), 250000 (\square), 404000 (\blacksquare) and 690000 (\triangle).

with a full width at half-maximum of 80 \AA), for a thin film of thickness h , diffusing into a semi-infinite medium given by

$$\phi(x) = 0.5 \operatorname{erf}[(h - x)/\sqrt{4Dt}] + 0.5 \operatorname{erf}[(h + x)/\sqrt{4Dt}], \quad (1)$$

where x is the distance away from the interface [16]. From the figure we can see that no segregation occurs to either CO_2 or the Si interfaces, even for the longest annealing times. Similar data was also obtained after annealing in scCO_2 along other (P, T) loci on the ridge. The D values are plotted on a log-log scale vs. molecular weight for each set of (P, T) values in fig 4. Here it should be noted that the film thickness of the top d-PS films was varied so as to satisfy the relation $L_0/R_g = 3$, where R_g is the polymer radius of gyration and the relation corresponds to the constant w_{co} values of 16.4%. This was done in order to eliminate any spurious effects due to chain confinement [10]. From the figure we can see that the four lines are parallel, each corresponding to the power law behavior $D = D_0 M^\alpha$ with $\alpha = -2.0$ along the density fluctuation ridge, which is identical to that for the entangled polymer melts above T_g [14, 17]. The data at each molecular weight was fit to an “effective” WLF form: $\log(D(T, P)/T) = A' - B'/(T - T'_\infty)$, where we obtained values for A' that scaled with M^2 , as expected, $B' = 22$, and $T'_\infty = 28^\circ\text{C}$ [18]. These values are much smaller than those reported for the bulk PS annealed above its T_g value, $B = 710$ and $T_\infty = 49^\circ\text{C}$ [15]. As can be seen in the inset of fig. 4, the WLF relationship (solid lines) provides a good fit to the data, indicating that the diffusion with the constant CO_2 concentration is temperature activated, as in the bulk. In this case the pressure is varied for each temperature so as to satisfy the relationship defining the ridge. This could be also seen in fig. 2(f) where we plot the diffusion coefficient at fixed $P = 8.2 \text{ MPa}$, as a function of temperature. The temperature dependence of D at $40 \leq T \leq 60^\circ\text{C}$ with $w_{\text{co}} \approx 10\%$ could be expressed as $\log(a_T) = \log(D_g/D) = -c_1(T - T_g)/(c_2 + T - T_g)$, where a_T is the shift factor, D_g is the observed D value at $T_g = 32^\circ\text{C}$ and $P = 8.2 \text{ MPa}$, $c_1 = 3.3$ and $c_2 = 36.6$. Although there is no data in terms of c_1 and c_2 for polymer- CO_2 systems, the trend for these parameters to be much smaller than those of bulk polymers [19] is similar to that for aqueous solutions of biological materials, such as glucose, sucrose and trehalose [20, 21]. Noted that a similar plot is shown in fig. 2(e), where the pressure dependence of the diffusion coefficient is plotted at

fixed $T = 36^\circ\text{C}$. Here we see that the diffusion of the thin film occurs only near the ridge because the anomalous solubility can be seen in the narrow region close to the ridge [2].

In conclusion, we have found that the anomalous swelling observed for PS thin films corresponds to a molten state ($T > T_g$) of the polymer that exists only near the density fluctuation ridge. In addition, we found that i) a combination of the anomalous sorption and plasticization effect, which were induced by the large density fluctuations in the solvent, was found to enhance the polymer interdiffusion by 2 orders of magnitude as the density fluctuation ridge was approached, and ii) even under the anomalous region, the diffusion occurs with the diffusion coefficients scaling as M^2 and follows an effective WLF relation, in the same manner as it does in an entangled melt above T_g .

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REFERENCES

- [1] MCHUGH M. A. and KRUKONIS V., *Supercritical Fluids Extraction Principles and Practice* (Woburn, MA) 1994.
- [2] KOGA T. *et al.*, *Phys. Rev. Lett.*, in press.
- [3] NISHIKAWA K., TANAKA I. and AMEMIYA Y., *J. Phys. Chem.*, **100** (1996) 418.
- [4] ARORA K. A., LESSER A. J. and MCCARTHY T. J., *Macromolecules*, **31** (1998) 4614.
- [5] STAFFORD C. M., RUSSELL T. P. and MCCARTHY T. J., *Macromolecules*, **32** (1999) 7610.
- [6] WISSINGER R. G. and PAULAITIS M. E., *J. Polym. Sci., Polym. Phys. Ed.*, **25** (1987) 2497.
- [7] GOEL S. K. and BECKMAN E. J., *Polymer*, **34** (1993) 1410.
- [8] WANG W. V., KRAMER E. J. and SACHSE W. H., *J. Polym. Sci., Polym. Phys. Ed.*, **20** (1982) 1371.
- [9] CONDO P. D., PAUL D. R. and JOHNSTON K. P., *Macromolecules*, **27** (1994) 365.
- [10] KOGA T. *et al.*, submitted to *Macromolecules*.
- [11] SCHWARZ S. A. *et al.*, *Mol. Phys.*, **76** (1992) 937.
- [12] CONDO P. D. *et al.*, *Macromolecules*, **25** (1992) 6119.
- [13] Assumed that the films are homogenous, SLD of d-PS-CO₂ mixture, SLD_{mix} can be expressed as a function of volume fraction of CO₂ (ϕ_{co}), *i.e.*, $\text{SLD}_{\text{mix}} = \text{SLD}_{\text{dps}} \times (1 - \phi_{\text{co}}) + \text{SLD}_{\text{co}} \times \phi_{\text{co}}$. The w_{co} values were then determined by $w_{\text{co}} = \rho_{\text{co}} \times \phi_{\text{co}} / (\rho_{\text{co}} \times \phi_{\text{co}} + \rho_{\text{dps}} \times (1 - \phi_{\text{co}}))$, where ρ is the density of each component in the mixture.
- [14] DOI M. and EDWARDS S. F., *The Theory of Polymer Dynamics* (Oxford Science, Oxford) 1986.
- [15] GREEN P. F. and KRAMER E. J., *J. Mater. Res.*, **1** (1986) 202.
- [16] CRANK J., *The Mathematics of Diffusion* (Oxford University Press, Oxford) 1975.
- [17] DE GENNES P. G., *J. Chem. Phys.*, **55** (1971) 572.
- [18] Since we observed the anomalous solubility enhancement in d-PS thin films on the ridge at $T > T_c$, the equation holds above T_c .
- [19] WILLIAMS M. L., LANDEL R. F. and FERRY J. D., *J. Am. Chem. Soc.*, **77** (1955) 3701.
- [20] KERR W. L. and REID D. S., *Lebensm.-Wiss. Technol.*, **27** (1994) 225.
- [21] MILLER D. P., DE PABLO J. J. and CORTI H. R., *J. Phys. Chem.*, **103** (1999) 10243.